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EFFECT OF RADIATION BLEACHING IN SODIUM-SILICATE GLASSES

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Radiation defects in the lattice of sodium-silicate glass that arise under the effect of γ -radiation were investigated by optical spectroscopy. Color centers of the hole type appeared in the glass at radiation doses in the $10^2 - 10^3$ Gy region.

Sodium-silicate glass is widely used in optics, industry, as bioactive additives in medicine, ornaments, etc. [1–3]. Addition of alloying dopants (Fe, Ti) [4] and exposure to high-energy radiation (x-ray, γ radiation) [2] are used for effectively altering the optical properties of glass. A detailed study of the mechanisms of formation of the radiation defects that arise after irradiation and alter the optical properties due to the appearance of electron and hole color centers in the glass will allow using these materials as radiation-resistant coatings, structures, and seals [5]. For this reason, we investigated the effect of γ radiation on the optical properties and radiation resistance of multicomponent sodium-silicate glass in the visible and ultraviolet regions of the spectrum. The trace element composition of the samples was (%): 0.0080 Pb, 0.0005 Cd, < 0.0020 Ni, < 0.0020 Co, 0.0006 Cu, 0.016 Zn, < 0.0020 Cr, 0.0002 Li, 0.0004 Rb, 0.0007 Cs, 0.0050 Sr. The chemical composition was (%): 73.80 SiO₂, 0.18 TiO₂, 1.90 Al₂O₃, 0.88 Fe₂O₃, 4.87 CaO, 3.93 MgO, 12.65 Na₂O, 0.72 K₂O, 0.03 P₂O₅, 0.04 MnO.

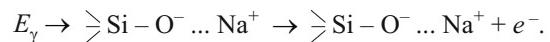
In irradiation of the glass with a γ -quanta beam of comparatively low energy ($E_\gamma \leq 10$ MeV), Compton scattering plays the predominant role, and the other effects comprise only a few percent [6]. The multicomponent sodium-silicate glasses investigated were irradiated with γ -quanta from a ⁶⁰Co source with energy of 1.25 MeV and rate of 1.3 Gy/min in the dose range of $D = 10^2 - 10^3$ Gy.

We know that the absorption spectrum of oxide glasses of the Na₂O–CaO–MgO–SiO₂ system can be described as the sum of the absorption bands of: L sites (edge of the UV region), Fe³⁺ (UV and visible regions), Fe²⁺ (UV, visible, and IR regions), OH[–] (IR region).

In studying the absorption spectra of unirradiated samples in the visible and UV regions (Fig. 1), two absorption bands in the 385 and 365 nm region were found. The first

band was induced by Fe³⁺ iron ions, which was confirmed by the published data [7, 8], and the second was due to so-called L sites, which bind with \geqslant Si–O[–] ... Na⁺ structural fragments [4, 9, 10].

The modifier ions in the glass lattice compensate for the negative charges on nonbridge oxygen ions [4]. L sites are excited during irradiation, and the oxygen ion in the O[–] state absorbs a γ quantum and passes into the O⁰ state with formation of L⁺ sites:



The presence of Na₂O in the glass lattice shift the band of the radiation-induced absorption caused by excitation of O[–] states and conversion to O⁰ from 620 nm (2 eV) to 465 nm (2.7 eV) [4]. As a consequence, the increase in absorption in the 450–530 nm region to $D = 1.3 \times 10^2$ Gy (see Fig. 1) and the subsequent decrease to saturation are due to nonbridge oxygen ions.

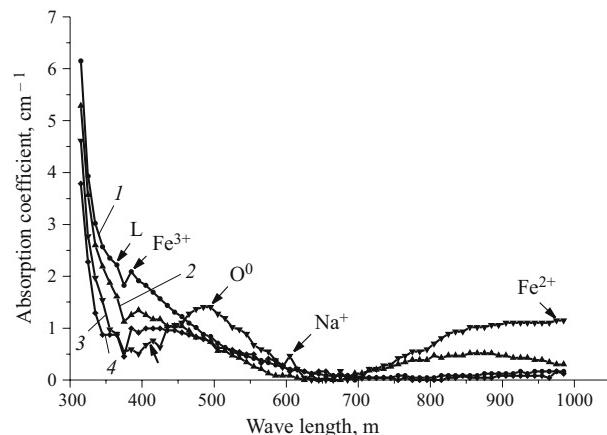


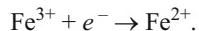
Fig. 1. Spectra of a sample before (1) and after (2–4) irradiation.

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After irradiation with a dose greater than 1.3×10^1 Gy, the samples turned yellow-brown, indicating the appearance of radiation color centers.

Previous studies [5] and a comparison with the data in [8] suggest that the change in the color of the samples was caused by color centers of the hole type induced by Na^+ ions localized on nonbridge oxygen ions. This was also confirmed by chemical analysis and the results of comparing the absorption spectra obtained before and after irradiation (see Fig. 1). During irradiation, the intensity of the absorption bands in the 415 and 615 nm region increased and consequently, the concentration of radiation defects caused by ionizing γ radiation also increased. At $D \geq 1.3 \times 10^2$ Gy, the values of the coefficients of the optical absorption band induced by Na^+ ions go out to the saturation level.

The electron freed as a result of the above reaction reacts with inherent defects in the glass lattice (Fe^{3+}) [4, 9] according to the reaction:



This explains the weakening of the intensity of the absorption band at 385 nm and the simultaneous increase in the intensity of the band with a maximum in the 1000 – 1100 nm region induced by Fe^{2+} ions during irradiation (Fig. 2). At the same time, Fe^{2+} valence electrons are knocked out and as a consequence, the valence changes from Fe^{2+} to Fe^{3+} as a result of exposure to the γ -quanta beam (Fig. 3).

A relaxation channel thus arises for the radiation excitation energy. The presence of iron in these multicomponent sodium-silicate glasses increases the radiation optical resistance of the glasses [4, 11].

With a further increase in the dose of radiation (more than $D \approx 1.3 \times 10^2$ Gy), a radiation bleaching effect is observed, consisting of an increase in absorption of induced losses before saturation and then a decrease in them (see Fig. 1, curve 4). The absorption spectrum at the given radiation dose contains the same absorption bands of L sites and Fe^{3+} as in the unirradiated sample. In the 315 – 500 nm region, the absorption diminished, while it did not change in the remaining region in comparison to the spectrum of the unirradiated sample, and this is due to the instability of the radiation color centers whose decomposition rate coincides with the trap filling rate in the formation of these centers [4]. This process was observed in quartz glasses at $D \geq 1.3 \times 10^2$ Gy [4]. The radiation bleaching effect in sodium-silicate glasses can be used for obtaining radiation-resistant materials with defined properties.

As a result of the study, we found that:

in irradiation with doses higher than $D \approx 1.3 \times 10^2$ Gy, a radiation bleaching effect is observed in sodium-silicate glasses;

the basic radiation-induced color centers that arise after γ -irradiation of sodium-silicate glasses are color centers of the hole type, induced by Na^+ ions and localized on nonbridge oxygen ions;

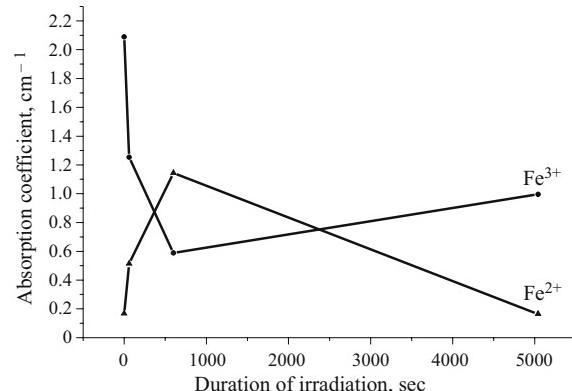


Fig. 2. Coefficients of optical absorption bands induced by Fe^{2+} and Fe^{3+} ions as a function of the radiation time.

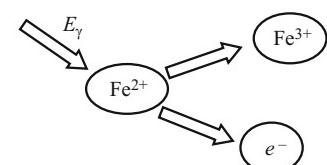


Fig. 3. Formation of Fe^{3+} ion from Fe^{2+} ion.

the presence of iron ions increases the radiation-optical stability of the glass due to the appearance of relaxation channels for radiation excitation energy.

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